

THE DESCRIPTION OF THE PROPERTY OF THE PROPERT

NOSC TR 587



Technical Report 587

NOSC TR 587

RESISTANCE OF COATED AND UNCOATED IR WINDOWS TO SEAWATER CORROSION PHASE IV

JD Stachiw (Naval Ocean Systems Center) SL Bertic (San Diego State University) Contract N00123-80-D-0554

1 October 1980

Final Report: October 1979-June 1980

Prepared for

Naval Electronic Systems Command

Approved for public release; distribution unlimited

岩

NAVAL OCEAN SYSTEMS CENTER SAN DIEGO, CALIFORNIA 92152

81 1 15 045



NAVAL OCEAN SYSTEMS CENTER, SAN DIEGO, CA 92152

AN ACTIVITY OF THE NAVAL MATERIAL COMMAND

SL GUILLE, CAPT, USN

Commander

HL BLOOD

Technical Director

ADMINISTRATIVE INFORMATION

Work was performed under 64515N, XO775-0S during the period October 1979 to June 1980, and was sponsored by Naval Electronic Systems Command.

Released by HR Talkington, Head Ocean Technology Department

METRIC CONVERSION

To convert from	to	Multiply by
inch	metre	2.540 X 10 ⁻²
foot	metre	3 048 X 10-1

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

NOSC Technical Report 587 (TR 587) A TITLE (and Substite) RESISTANCE OF COATED AND UNCOATED IR WINDOWS TO SEAWATER CORROSION. PHASE IV. 2. AUTHOR(a) JD Stachiw 10. Stachiw 10. San Diego State University 3. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Ocean Systems Center San Diego, CA 92152 11. CONTROLLING OFFICE NAME AND ADDRESS Naval Electronic Systems Command Washington, DC 20360 12. MONITORING AGENCY NAME & ADDRESS(11 ditterent from Controlling Office) 18.	PERFORMING ORG. REPORT NUMBER CONTRACT OR GRANT NUMBER (A) PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS (A515N X0775 US REPORT DATE 1 October 180 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified DECLASSIFICATION/DOWNGRADING SCHEDULE
RESISTANCE OF COATED AND UNCOATED IR WINDOWS TO SEAWATER CORROSION. PHASE IV. 2. AUTHOR(1) JD Stachiw HOSE SL Bertic San Diego State University 3. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Ocean Systems Center San Diego, CA 92152 11. CONTROLLING OFFICE NAME AND ADDRESS Naval Electronic Systems Command Washington, DC 20360 14. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office) 15. 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	PERFORMING ORG. REPORT NUMBER CONTRACT OR GRANT NUMBER(e) N00123-80-D-0554 PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 64515N X0775 US REPORT DATE 1 October 1980 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
RESISTANCE OF COATED AND UNCOATED IR WINDOWS TO SEAWATER CORROSION. PHASE IV. 2. AUTHOR() JD Stachiw HOSE SL Bertic San Diego State University 9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Ocean Systems Center San Diego, CA 92152 11. CONTROLLING OFFICE NAME AND ADDRESS Naval Electronic Systems Command Washington, DC 20360 14. MONITORING AGENCY NAME & ADDRESS(it different from Controlling Office) 15. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	PERFORMING ORG. REPORT NUMBER CONTRACT OR GRANT NUMBER(e) NO0123-80-D-0554 PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 64515N XO775 0S REPORT DATE 1 October 980 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
TO SEAWATER CÓRROSION. PHASE IV. 1. AUTHORA: JD Stachiw MOSE SL Bertic San Diego State University 9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Ocean Systems Center San Diego, CA 92152 11. CONTROLLING OFFICE NAME AND ADDRESS Naval Electronic Systems Command Washington, DC 20360 12. 13. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office) 15. 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	PERFORMING ORG. REPORT NUMBER CONTRACT OR GRANT NUMBER(*) N00123-80-D-0554 PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 64515N XO775 0S REPORT DATE 1 October 980 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
TO SEAWATER CÓRROSION. PHASE IV. 1. AUTHORA: JD Stachiw MOSE SL Bertic San Diego State University 9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Ocean Systems Center San Diego, CA 92152 11. CONTROLLING OFFICE NAME AND ADDRESS Naval Electronic Systems Command Washington, DC 20360 12. 13. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office) 15. 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	PERFORMING ORG. REPORT NUMBER CONTRACT OR GRANT NUMBER(*) N00123-80-D-0554 PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 64515N XO775 0S REPORT DATE 1 October 980 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
JD Stachiw NOSE SL Bertic San Diego State University PERFORMING ORGANIZATION NAME AND ADDRESS Naval Ocean Systems Center San Diego, CA 92152 11. CONTROLLING OFFICE NAME AND ADDRESS Naval Electronic Systems Command Washington, DC 20360 14. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office) 15. 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	CONTRACT OR GRANT NUMBER(s) N00123-80-D-0554 PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 64515N X0775 0S REPORT DATE 1 October 1980 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
ID Stachiw NOSE SL Bertic San Diego State University PERFORMING ORGANIZATION NAME AND ADDRESS Naval Ocean Systems Center San Diego, CA 92152 11. CONTROLLING OFFICE NAME AND ADDRESS Naval Electronic Systems Command Washington, DC 20360 14. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office) 15. 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 64515N XO775 0S REPORT DATE 1 October 980 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
SL Bertic San Diego State University PERFORMING ORGANIZATION NAME AND ADDRESS Naval Ocean Systems Center San Diego, CA 92152 11. CONTROLLING OFFICE NAME AND ADDRESS Naval Electronic Systems Command Washington, DC 20360 14. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office) 15. 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 64515N XO775 US REPORT DATE 1 October 1980 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
San Diego State University Performing Organization name and address Naval Ocean Systems Center San Diego, CA 92152 11. Controlling Office name and address Naval Electronic Systems Command Washington, DC 20360 14. Monitoring agency name & address(it different from Controlling Office) 15. 16. Distribution statement (of this Report) Approved for public release; distribution unlimited.	PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 64515N X0775 US REPORT DATE 1 October 1980 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
Naval Ocean Systems Center San Diego, CA 92152 11. CONTROLLING OFFICE NAME AND ADDRESS Naval Electronic Systems Command Washington, DC 20360 14. MONITORING AGENCY NAME & ADDRESS(it different from Controlling Office) 15. 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	AREA & WORK UNIT NUMBERS 64515N X07750S REPORT DATE 1 October 1989 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
Naval Ocean Systems Center San Diego, CA 92152 11. CONTROLLING OFFICE NAME AND ADDRESS Naval Electronic Systems Command Washington, DC 20360 14. MONITORING AGENCY NAME & ADDRESS(it different from Controlling Office) 15. 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	AREA & WORK UNIT NUMBERS 64515N X07750S REPORT DATE 1 October 1989 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
San Diego, CA 92152 11. CONTROLLING OFFICE NAME AND ADDRESS Naval Electronic Systems Command Washington, DC 20360 14. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office) 15. 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	REPORT DATE 1 October 180 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
Naval Electronic Systems Command Washington, DC 20360 14. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office) 15. 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	REPORT DATE 1 October 1980 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
Naval Electronic Systems Command Washington, DC 20360 14. MONITORING AGENCY NAME & ADDRESS(II different from Controlling Office) 15. 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	1 October 1980 NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
Washington, DC 20360 14. MONITORING AGENCY NAME & ADDRESS(it different from Controlling Office) 15. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	NUMBER OF PAGES 39 SECURITY CLASS. (of this report) Unclassified
Washington, DC 20360 14. MONITORING AGENCY NAME & ADDRESS(it different from Controlling Office) 15. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	39 SECURITY CLASS. (of this report) Unclassified
14. MONITORING AGENCY NAME & ADDRESS(it different from Controlling Office) 15. 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.	Unclassified
Approved for public release; distribution unlimited.	
Approved for public release; distribution unlimited.	DECLASSIFICATION/DOWNGRADING SCHEDULE
Approved for public release; distribution unlimited.	30160016
Approved for public release; distribution unlimited.	
17. DISTRIBUTION STATEMENT (of the obstract entered in Block 20. If different from Re	
17. DISTRIBUTION STATEMENT (of the ebetract entered in Block 20. If different from Re	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20. If different from Re	
Piet illes ileit et et ement i for une engages autores un engage est il griss en autori	sport)
18. SUPPLEMENTARY NOTES	
<i>₹</i>	
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)	
Antireflective coating	
Germanium	-
Infrared windows	
Seawater corrosion	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)	
Germanium and chalcogenide glass specimens were submerged to a 35-for	ot denth in San Diego Roy for 130 de
and the deterioration of their surfaces noted. The germanium specimens were	
antireflective infrared (IR) coatings, or with chalcogenide glass protective coa	
specimens were tested bare.	
The submerged specimens were subjected to a forced water circulation at	annroximately 6-feet-ner-second
velocity to simulate actual operational scenarios to which a submarine-mount	
(continued on reverse side)	

DD 1 FORM 1473

EDITION OF 1 NOV 65 IS OBSOLETE S/N 0102-LF-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered)

(continued from block 20).

The chalcogenide AMTIR-1 glass specimens and the germanium specimens protected by the chalcogenide glass coating XF206 from Optic Electronic exhibited excellent corrosion resistance. The multilayer durable antireflection (AR) 40100 from Exotic Materials, although not as corrosion resistant as chalcogenide glass coating, exhibited the best corrosion resistance of all AR coatings tested in this study.

Other AR coatings on germanium deteriorated to different degrees. The severest deterioration took place on a germanium specimen covered with multilayer coating (the Optic Electronic XF204), but even there the transmission decreased only by approximately 5 percent, in the presence of many shallow (© 0.010-inch) and few deep (© 0.030-inch) corrosion craters in the surfaces of the germanium specimens.

Carbon coatings, because of their potential resistance to seawater and abrasion, have been selected as the next class of coatings for evaluation in seawater environment.

- 4 01 =

Acces	sion For			
	GRA&I	X		
DTIC	TAB			
Unann	iounced			
Justification				
Ву				
Distr	ribution/	' · _ · _ · _ · _ · _ · _ · 		
Avai	.lability	Codes		
<u> </u>	Avail a	nd/or		
Dist	Specia	al.		
A				

PROBLEM

A germanium window in submarine-mounted infrared (IR) imaging systems is immersed in seawater during most of its operational life. Germanium corrodes in seawater and it is therefore necessary to develop a method of protecting the germanium. This method of protection, however, must not interfere with, but if feasible must assist, the function of the imaging systems. Therefore, the protective coating on the external surface of the window must not impede, but must enhance the transmission of electromagnetic radiation in the 8- to 12-micron spectral wavelength range.

APPROACH

An experimental approach to the problem was taken, involving the testing of various types of coatings on specimens fabricated from germanium and chalcogenide glass.

Specifically, the specimens were tested by exposure to seawater, with forced circulation generated by a submersible pump. Forced circulation was utilized to approximate actual operational scenarios and to discourage biological fouling.

The specimens tested were of four types: AMTIR-1 glass, germanium with the Exotic Materials multilayer durable AR coatings, germanium with the Optic Electronic single layer and multilayer AR coatings, and germanium with the Optic Electronic chalcogenide coating.

The testing took place from 31 January to 11 June 1980, in San Diego Bay off Berthing Pier 160, NOSC, Bayside, at a 35-foot depth.

RESULTS

The test specimens were wetted by seawater on one face only, and this surface was cleaned and dried after removal from the ocean environment and prior to transmission testing. The following findings were formulated on the basis of observations made during the testing:

- 1. The specimens of AMTIR-1 chalcogenide glass and the germanium specimen coated with chalcogenide glass (Optic Electronic XF206) showed no signs of corrosion and suffered no loss in transmission after 130 days' exposure to seawater.
- 2. The germanium specimen coated with the Exotic Materials 40100 remained in very good condition, less than 2 dozen pinpoint pits were observed at termination of test period, and there was no measurable decrease in transmission over the 8- to-12-micron-wavelength range.
- 3. The specimens coated with Optic Electronic XF203 and XF204 gave the poorest performance in terms of transmission loss, with the XF204 showing not only the largest transmission loss but also the most damage from pitting and corrosion.
- 4. The remainder of the AR coated specimens showed relatively similar minor losses in transmission and varying minor amounts of corrosion, better than the specimen coated with OE XF 204, but less promising than the specimen coated with EM 40100.

CONCLUSION

1. Multilayer antireflective coatings deposited on germanium windows can reliably protect the surface of germanium windows from significant corrosive action of flowing

seawater for periods in excess of 130 days. The best multilayer AR coating tested loses less than 1 percent of its original transmission capability over the 6- to-13-micron-wavelength range during that time period.

- 2. Chalcogenide glass AMTIR-1 possesses excellent resistance to seawater corrosion, and thus does not require any protective coatings on the wetted face. There was no measureable decrease in transmission after a 130-day submersion in flowing seawater. The projected service life of AMTIR-1 chalcogenide glass windows in marine environment is at least one year, and probably several years.
- 3. Germanium coated with chalcogenide glass shows excellent resistance to corrosion and there is no measurable decrease in transmission after a 130-day submersion in seawater.

RECOMMENDATIONS

Applied research on preventing corrosion of IR windows in shipmounted IR systems should focus on the promising leads developed in this study on the utilization of chalcogenide glass as either the primary window material, or as a coating for germanium, since both approaches have the potential of extending significantly the service life of IR windows in marine environment past the longest documented life expectancy of premium multilayer AR coatings.

It is preferable to employ chalcogenide glass as primary window material rather than as a protective coating for germanium, since the transmission through massive chalcogenide glass coated only on the nonwetted surface with a standard AR coating is 10 to 20 percent higher than through germanium coated on the nonwetted surface with standard AR coating and protected on the exterior surface from corrosive attack of seawater by a thick chalcogenide glass layer.

Basic research on corrosion resistant coatings should be directed toward application to germanium of thick carbon layers with diamond-like molecular structures. If generation and application of carbon coatings becomes feasible, the resulting coatings should prove to be superior to chalcogenide glass coatings in antireflection characteristics and scratch resistance. Dr TJ Moravec at the Honeywell Technology Center, Bloomington, Minnesota has already succeeded in applying hard carbon coatings to 3-inch-diameter germanium windows. The resultant transmission through 0.25-inch-thick germanium windows, coated only on a single face, was 60 to 65 percent in the 8- to 12-micron-wavelength range.

CONTENTS

INTRODUCTION page 3
STUDY PROCEDURE 4
TEST PREPARATION 4
Test Specimens 4 Test fixture 4 Test arrangement 11 Test procedures 11
FINDINGS 17
TRANSMISSION MEASUREMENTS 32
CONCLUSIONS 39
RECOMMENDATIONS 39 Technical 39
REFERENCES 40

INTRODUCTION

All infrared (IR) imaging systems operating in a marine environment require for their successful performance windows that, besides being transparent to infrared radiation, are also compatible with environmental parameters imposed by the marine environment. The environmental parameters inherent to submerged operations present a particularly difficult challenge to the designer of such an optical component as the window. For, in addition to being transparent in the IR energy spectrum and resistant to salt water corrosion, the window must also serve as a structural element of the pressure housing protecting other electro-optical imaging components from seawater intrusion.

Even windows that successfully carry the structural loads imposed on them by hydrostatic loading must still face the prolonged chemical attack of seawater on the highly polished surfaces exposed to the marine environment. Although germanium is not a very active chemical material, seawater reacts with it and forms soluble oxides and chlorides on its surface. For this reason, bare germanium windows cannot be used in marine service because the rough, corroded surface scatters and reflects incident thermal energy, significantly decreasing the strength of thermal signal transmitted through the window. With these restraints in mind, the options available to the designer are:

- 1. Replace germanium with a more corrosion-resistant material transparent to infrared radiation.
- 2. Develop AR coatings for germanium with higher corrosion resistance.
- 3. Protect the germanium with a corrosion resistant surcoat transparent to infrared radiation.

Earlier testing (references 1, 2 and 3) has indicated that one previous option, a protective surcoat of a plastic material, provided largely negative results in protecting AR coated windows. The various plastic surcoats tested showed neither the film uniformity, nor the ease of application, nor the lasting adhesion necessary to provide such protection. The indication from previous testing was that the areas of greatest potential are:

- 1. Development of hardier multilayer AR coatings.
- 2. Development of surcoats from proven corrosion resistant materials transparent in the 8- to-12-micron range.

This report summarizes the study undertaken at NOSC to evaluate the potential for improvement in these approaches for preventing window corrosion in marine environment IR systems.

^{1.} Naval Ocean Systems Center Technical Note 121, Undersea Testing of IR Antireflective Coatings and IR Materials, by JN Ferrer, March 1977.

^{2.} Naval Ocean Systems Center Technical Report 421, Resistance of Coated and Uncoated IR Windows to Seawater Corrosion, by JD Stachiw and SL Bertic, August 1979.

^{3.} Naval Ocean Systems Center Technical Report 572, Resistance of Coated and Uncoated IR Windows to Seawater Corrosion, Phase III, by JD Stachiw and SL Bertic, July 1980.

STUDY PROCEDURE

The objective of the study was to evaluate, in the shortest possible time and with the least expenditure of funds, the potential return of each of the approaches mentioned previously to extend the life of IR windows in marine service.

The approach to this study was experimental. It consisted of selecting representative samples of each of the options available and submerging them in the ocean. At regular intervals, the specimens were retrieved from the ocean and their condition noted.

The scope of the study was limited in number of test specimens, AR coatings and alternate materials, and by the results of previous phases of testing. As a result of this limitation, only the following potential approaches to increasing the life of IR windows in an ocean environment were to be evaluated:

- 1. Alternate materials:
 - a. Chalcogenide glass AMTIR-1
- 2. Competitive AR coatings for germanium
 - a. Multilayer durable antireflective coating applied to germanium by Exotic Materials
 - b. Multilayer antireflective coating applied to germanium by Optic Electronic
 - c. Single layer antireflective coating applied to germanium by Optic Electronic
- 3. Protective surcoats for IR materials:
 - a. Chalcogenide glass overcoat applied to germanium by Optic Electronic.

The test procedure called for continuous submersion of 130 days in seawater, the maximum duration of a typical submarine mission. The ambient environment was limited to only two conditions: forced water circulation (pump operating), and natural circulation (pump not operating). The specimens were alternately subjected to each of these conditions, spending 50 percent of each week under each condition, both submerged to 35 feet. The natural circulation of seawater was to simulate the flow of water encountered by a typical IR system in retracted position inside the sail of a submarine, while the forced circulation was to simulate the flow of seawater past the IR system when the sensor mast was in either a partially or fully extended position.

TEST PREPARATION

TEST SPECIMENS

All specimens tested were 3-inch diameter, 0.25-inch-thick circular disks with polished faces (figure 1). There were 10 specimens of germanium with various coatings, and 2 specimens of AMTIR-1 glass. An inventory of the specimens used can be found in table 1 of this report.

TEST FIXTURE

The test fixture used in this experiment held twelve specimens to be tested for fouling and corrosion with forced water circulation. The specimen holder for the fixture was a polyvinylchloride (PVC) sheet, $21.00 \times 16.00 \times 1.00$ inches. It had twelve evenly spaced recesses for specimens which, after mounting, were flush with the surface of the PVC plate. Each recess had a 0.25-inch-wide seat around the circumference that the specimen rested on, and a shallow cavity below the specimen. The sheet had evenly spaced holes in it to accommodate the PVC studs for fixture assembly.

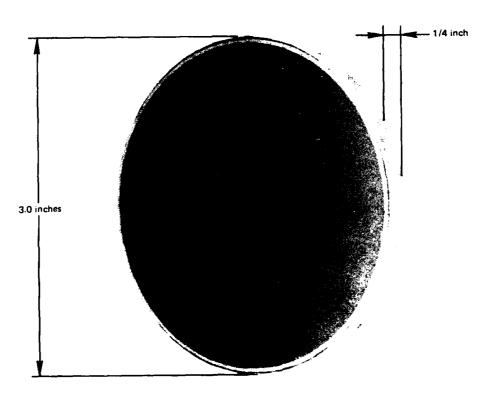


Figure 1. A γ pical specimen. This one is coated, showing the side exposed to seawater.

Specimen		Coating		
Number	Manufacturer	Sea Face	Dry Face	
59	AMTIR	None	None	
60	AMTIR	None	None	
65	Exotic Materials	AR-40100 None (Multilayer Durable)		
66	Exotic Materials	AR-40100 None (Multilayer Durable)		
76	Optic Electronic	AR-XF 127	None	
80	Optic Electronic	AR-XF 204	None	
81	Optic Electronic	AR-XF 205	None	
82	Optic Electronic	AR-XF 202	None	
83	Optic Electronic	AR-XF 203	None	
84	Optic Electronic	AR-XF 203	None	
85	Optic Electronic	AR-XF 205	None	
86	Optic Electronic	XF206 (chalcogenide glass	None s)	

Table 1. Specimens tested with forced circulation.

Each specimen was placed in the fixture on two nylon fiber reinforced neoprene gaskets that fit on the specimen seat. The specimen was then fastened watertight with an 0-ring held down by a titanium ring clamp fastened with nylon screws (figure 2).

A 0.50-inch-thick acrylic sheet was placed on either side of the specimen holder as a protective cover for the specimens. The acrylic sheets were drilled in the same manner as the specimen holder so that the studs would pass through them. The acrylic sheets were fastened in place with 0.50-inch PVC washers and hex nuts. Additionally, the acrylic sheet over the specimens was fitted with a device to provide forced circulation (figure 3). The device consisted of a Blue Cascade Submersible Pump, model B1-000, which circulated seawater through a manifold. The manifold was made of 0.50-inch copper pipe with brass fittings. The pipes passed through holes in the acrylic plate centered above each specimen. The manifold was secured to the acrylic sheet by fittings on the specimen side of the acrylic plate, which acted as nozzles that directed streams of water at the centers of the specimens.

The arrangement of water flow in the manifold, combined with various-diameter apertures in pipe caps placed on the nozzles, provided for the adjustment of the twelve water jets to the desired water velocity of 6 feet per second. When the acrylic plate and manifold were placed over the studs, the tubular spacers provided a 0.75-inch stand-off for the water nozzles above the specimens (figures 4 and 5).

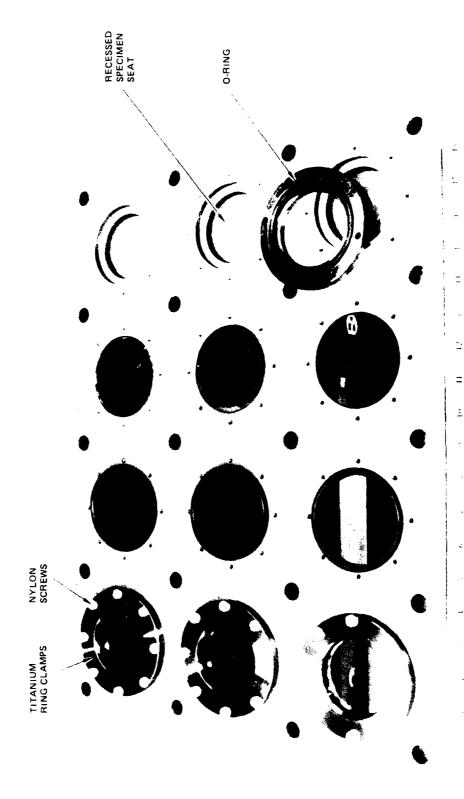


Figure 2. Multiple specimen test fixture in process of assembly.

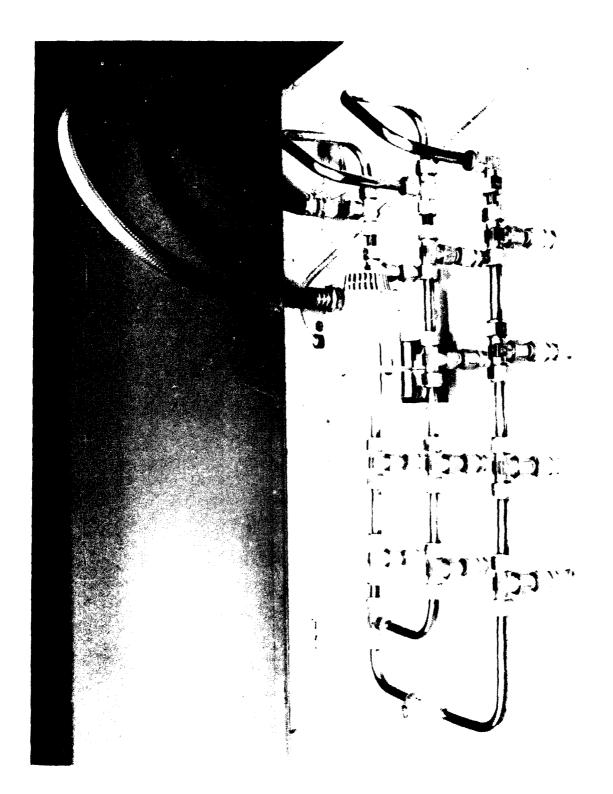


Figure 3. The pump and manifold apparatus for the provision of forced circulation, attached to a protective acrylic plate.

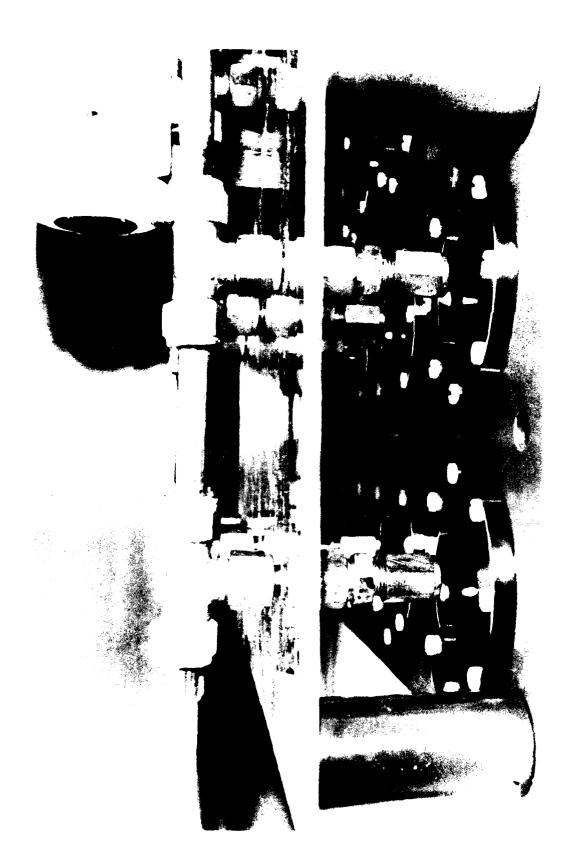


Figure 4. The forced circulation apparatus in place above the specimens in the test fixture.

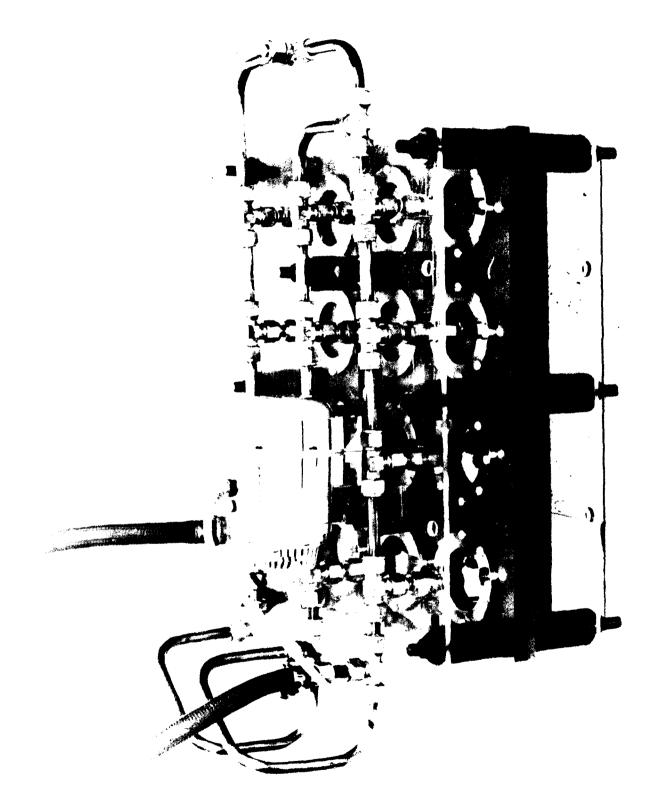


Figure 5. The assembled test fixture with the forced circulation apparatus in place on top.

TEST ARRANGEMENT

The testing took place off Berthing Pier 160 using the Sonar Facility located in building 160B, NOSC, Bayside, which houses a hydraulically operated hoist that was used for lowering the specimens into San Diego Bay. The hoist is a flat platform to which the fixture was attached. That platform is on a cart which moves along tracks set at a 30-degree inclination to the water's surface (figure 6). The cart is raised or lowered by means of cables on a rotating drum driven by a hydraulic motor (figure 7).

The pump on the fixture was connected in series through a 0-10-ampere Simpson ammeter to the outlet in Building 160B, rated at 20 ampere, 220 volt maximum. Ocean, temperature readings were taken with a mercury column thermometer, with a -15 to +65 degrees Celsius scale.

TEST PROCEDURES

The specimens, which are listed in table 1, were arranged in the fixture for data collection (figure 8). The assembled fixture was lowered into the bay and the testing commenced 31 January 1980. Data from each specimen were recorded, including day of the test, and qualitative visual observations of growth on, and physical condition of, the specimen (figure 9). Also noted were the currents that the pump was drawing and whether water was flowing from the manifold. Further, the data included description of ocean conditions such as water temperature, tide induced water circulation, water surface conditions, and sunlight conditions.

For the duration of the test, the fixture was raised once or twice per week for inspection. Photographic documentation of the specimens' surfaces was taken before testing was initiated, and at the end of each month of testing. Excess marine growth was periodically hosed from the fixture (figure 10), and cleared from the pump intake.

During the weekly inspections the specimens were not removed from their mountings. These periodic visual inspections focused on the degree of fouling, depth of corrosion pits, and extent of pitting.

After conclusion of testing in the bay, surfaces of all specimens were thoroughly cleaned to prepare them for IR transmission tests.

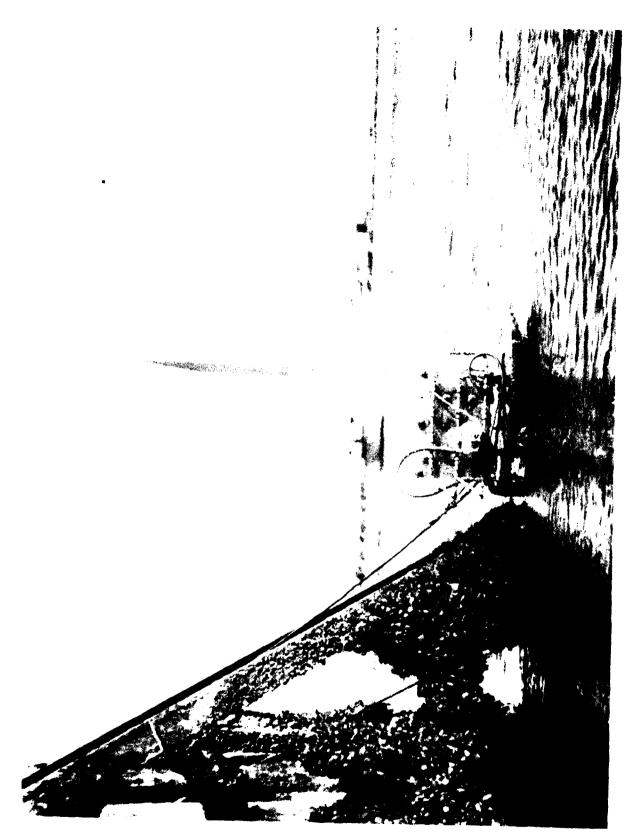
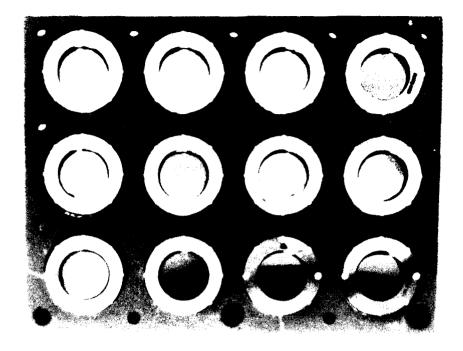


Figure 6. The test fixture affixed to the testing platform, and the tracks of the hydraulic lift the platform runs on,



Figure 7. The hydraulic lift platform with the test fixture attached, at the top of the lift tracks.



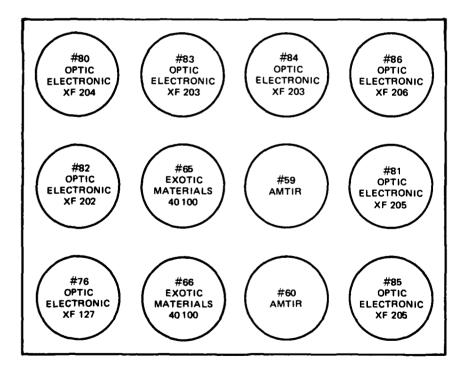


Figure 8. The arrangement of the specimens in the test fixture. The photograph was taken prior to immersion.



Figure 9. The specimens were periodically removed from the bay and qualitative visual observations were made and recorded.



Figure 10. Marine growth was periodically hosed off of the fixtures.

FINDINGS

The only germanium specimen that did not visibly deteriorate within the four-month testing period was the specimen protected by the Optic Electronic chalcogenide glass surcoat OEC XF 206 (figure 11). The specimen had no signs of pitting, corrosion or discoloration, although it suffered a small scratch and chip in its surface during cleaning and removal from the test fixture.

The two specimens of AMTIR-1 chalcogenide glass also remained in excellent condition throughout the testing period (figure 12). One of the two specimens had some fine superficial scratches, probably incurred during the cleaning operation, otherwise there was no visible change.

Showing some minor signs of deterioration, yet still in an outstanding condition after the four-month testing period, were the two germanium specimens protected by multilayer antireflective EM 40100 coating. These specimens had developed some minor pinpoint pitting by the end of the second month, each having approximately one dozen fine pits by that time (figure 13). Only a very slight increase in pitting occurred in the final two months, culminating in several dozen very shallow (≤ 0.001 -inch) pits per specimen. There was no discoloration of the coating (figure 14.)

The specimen protected with Optic Electronic XF 202 AR coating exhibited shallow craters. The specimen began to pit after the first month of testing, and by the second month it had approximately 30 pinpoint pits (figure 15). The pitting increased slightly in severity during the following months of testing and by the end of the testing period there were approximately 75 to 100 shallow (≤ 0.010 -inch), small diameter (≤ 0.020 -inch) craters concentrated near the center of the specimen directly under the nozzle (figure 16).

Similarly, the two specimens coated with the Optic Electronic XF 203 coating had about 3 dozen pinpoint pits each by the second month (figure 17), which increased to 60 to 100 very fine pits by the end of the test period (figure 18). Among those were 20 to 30 shallow (≤ 0.010 -inch), small-diameter (≤ 0.020 -inch) craters. Both of the XF 203 specimens sustained mild discoloration concentrated at the centers of the specimens, and spreading over most of their surfaces.

The specimen with the Optic Electronic XF 127 coating sustained only 3 or 4 pinpoint pits during the testing period, but it began to discolor by the second month of testing (figure 19). The discoloration increased to cover 90 percent of the surface of the specimen with lighter colored blotches by the end of the testing period (figure 20).

The two specimens with the Optic Electronic XF 205 coating were also discolored. They started to discolor within the first month near the centers of the specimens, and discoloration continued into the second month (figure 21). By the end of the third month, one of the specimens had a couple of pinpoint pits starting, and by the end of the testing period the specimens were discolored over 85 to 100 percent of their surfaces, and one of them had three or four small pits (figure 22).

The specimen exhibiting the poorest resistance to seawater corrosion was the one coated with Optic Electronic XF 204. The specimen began to discolor shortly after the first month of testing, and by the second month of testing there was extensive pinpoint pitting on the surface (figure 23). By the end of the testing period the specimen had more than 400 craters, the deepest approximately 0.030 inch. This specimen also was discolored over about 50 percent of its surface (figure 24).

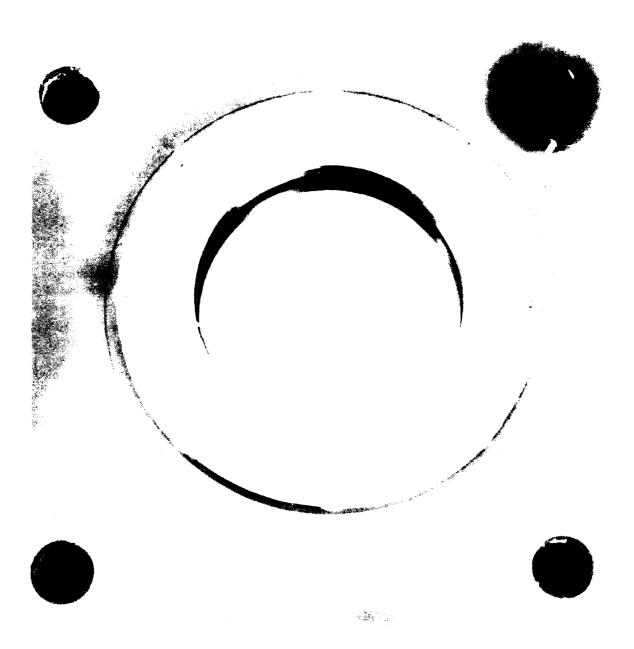


Figure 11. A specimen with the Optic Electronic XF 206 AR coating after four months of testing in San Diego Bay.

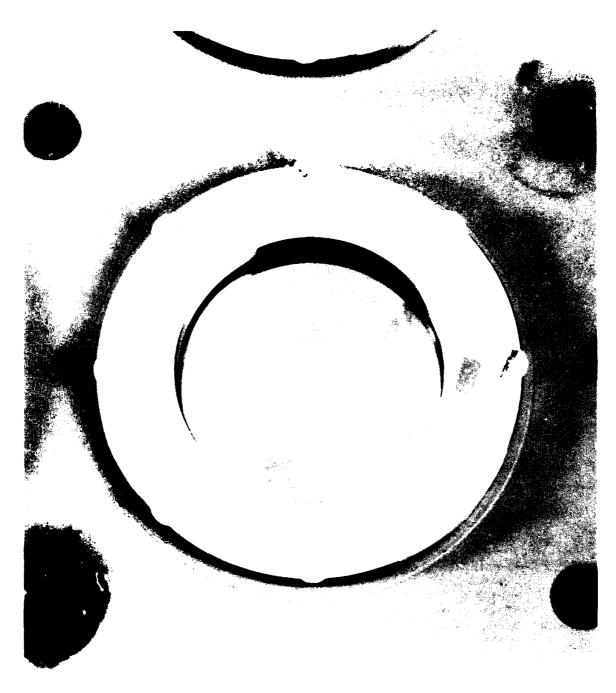


Figure 12. A specimen of AMTIR glass after four months of testing in San Diego Bay.



Figure 13. A specimen with the Exotic Materials 40100 AR coating after two months of testing in San Diego Bay.

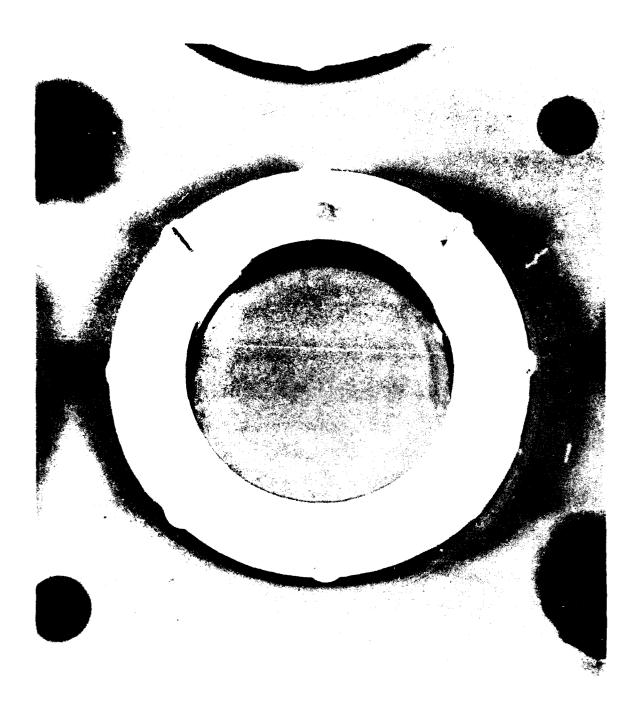


Figure 14. A specimen with the Exotic Materials 40100 AR coating after four months of testing in San Diego Bay.



Figure 15. A specimen with the Optic Electronic XF 202 AR coating after two months of testing in San Diego Bay.

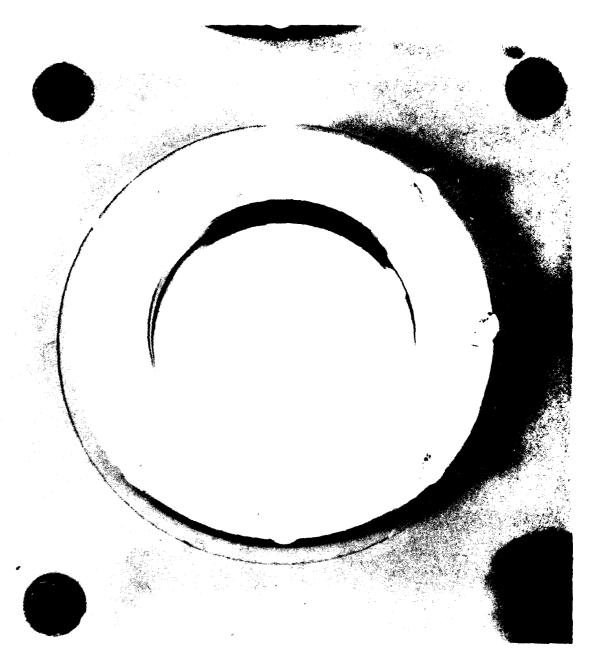


Figure 16. A specimen with the Optic Electronic XF 202 AR coating after four months of testing in San Diego Bay.

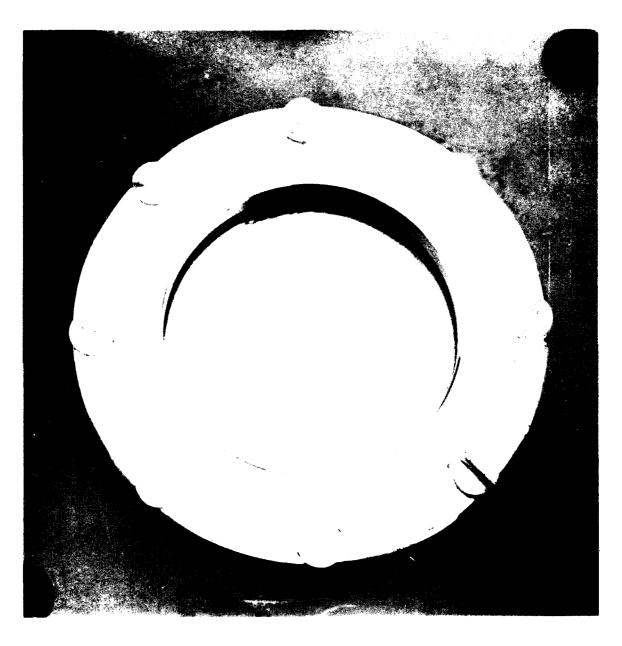


Figure 17. A specimen with the Optic Electronic XF 203 AR coating after two months of testing in San Diego Bay.



Figure 18. A specimen with the Optic Electronic XF 203 AR coating after four months of testing in San Diego Bay.

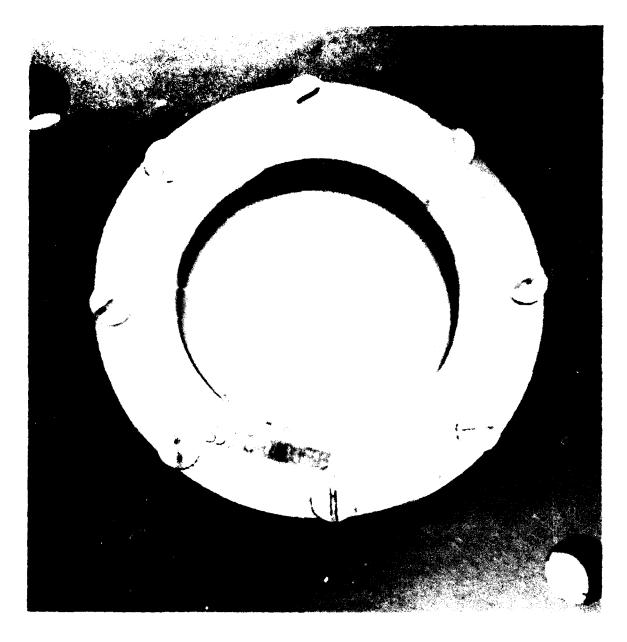


Figure 19. A specimen with Optic Electronic XF 127 AR coating after two months of testing in San Diego Bay.

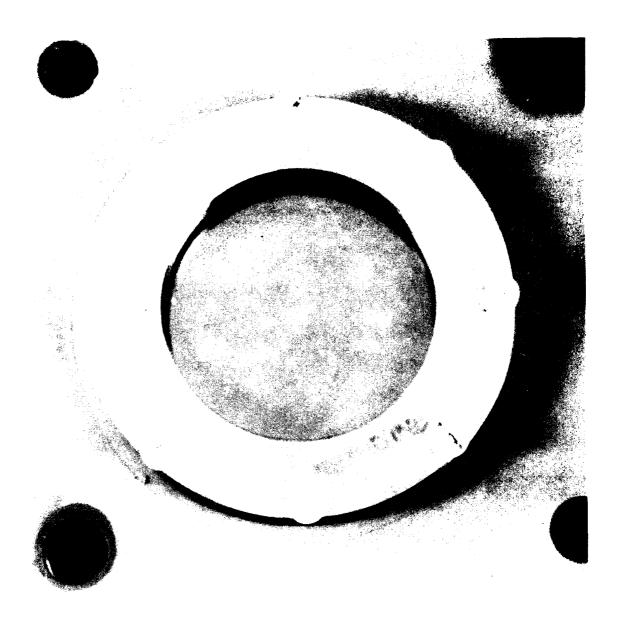


Figure 20. A specimen with the Optic Electronic XF 127 AR coating after four months of testing in San Diego Bay.



Figure 21. A specimen with the Optic Electronic XF 205 AR coating after two months of testing in San Diego Bay.



Figure 22. A specimen with the Optic Electronic XF 205 AR coating after four months of testing in San Diego Bay.

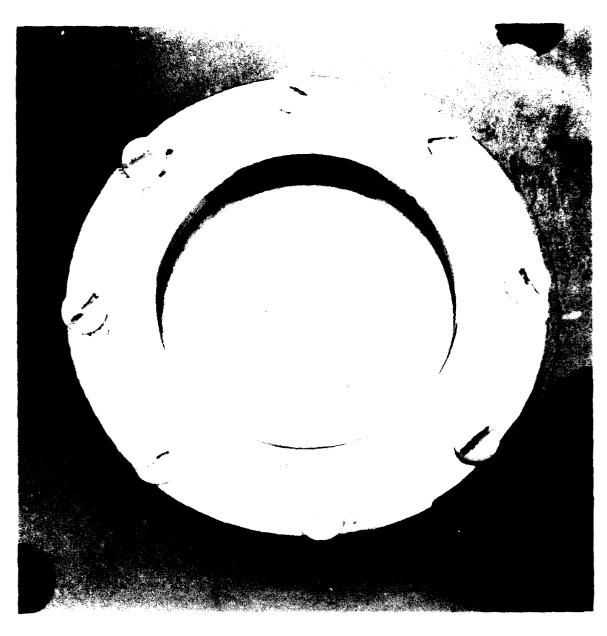


Figure 23. A specimen with the Optic Electronic XF 204 AR coating after two months of testing in San Diego Bay.

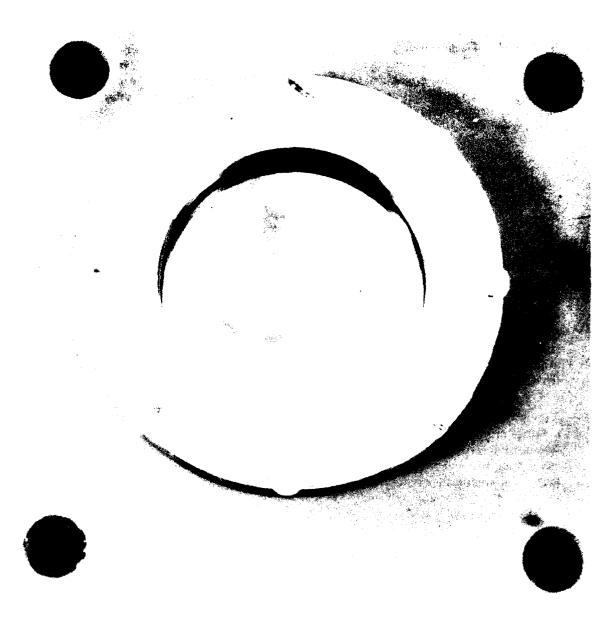


Figure 24. A specimen with the Optic Electronic XF 204 AR coating after four months of testing in San Diego Bay.

The discolorations of coatings observed on some of the test specimens revealed themselves upon closer inspection as widespread leaching away of layers composing the anti-reflection coatings. This mechanism of surface deterioration differs significantly from the other mechanisms of surface deterioration observed on some of the specimens where the coating, instead of widespread leaching, develops local pinholes through which the seawater subsequently attacks the germanium substrata. Of these two mechanisms of corrosion the widespread leaching out of coating layers decreases the optical transmission more than highly localized formation of deep pits or craters. From the maintenance viewpoint, however, the leaching out of coating is a much less destructive form of corrosion; during refinishing of such windows less, or none, of germanium substrata need be removed prior to recoating. This is not the case with pitted surfaces where 0.020 to 0.060 inch of germanium substrata must be ground off before the surface can be polished and recoated.

TRANSMISSION MEASUREMENTS

Transmission tests were performed on all the specimens to compare the effectiveness of the various coatings before and after submersion in seawater. Both measurements were performed on specimens whose surfaces were cleaned and dried. The measurements provide data on the transmission of electromagnetic radiation in the 6- to 14-micron-wavelength range only. The effect of surface deterioration on the mean transfer function (MTF) of the specimens was not measured, and thus it is not known how much the optical resolution of a thermal imaging system would suffer if it were equipped with windows coated in the same manner as the test specimens exposed to a seawater environment.

Of the specimens tested, only one coated with the Optic Electronic XF 204 showed a drop in transmittance, after a 4-month submersion in seawater, that exceeded 5 percent over the whole range of measurement (figure 25). The after exposure to seawater transmittance curve of the specimen ranged from 55% transmittance at the lower end (6-micron wavelength) of the spectrum, to 36% transmittance at the 14-micron wavelength, in a reasonably smooth trace.

The specimen with the Optic Electronic XF 127 coating (figure 26) also showed a drop in transmittance of about 5% in the lower to middle wavelength range, but the transmittance drop was less in the higher middle range (10 to 12 microns wavelength). The transmission varied, after a 4-month exposure to seawater, from a low of 48% at 6-micron wavelength, to a high of almost 60% in 8- to 11-micron range, with a 4% dip in 9- to-10-micron range. The transmittance steadily dropped from the 11-micron point in the wavelength spectrum, to a low of approximately 40% at 14-micron wavelength.

The remaining specimens had only very small changes in percent transmittance after exposure to seawater.

The AMTIR-1 chalcogenide glass showed no significant change, averaging 68% transmittance from 6- to 11-micron wavelength, and slightly dropping from that point to a transmittance of 55% at 14-micron wavelength (figure 27). The transmittance of the Exotic Materials 40100 coated specimen also remained significantly unchanged (figure 28). It dropped after testing only in the 13- to 14-micron-wavelength range, and then by a maximum of 5% at 14-micron wavelength.

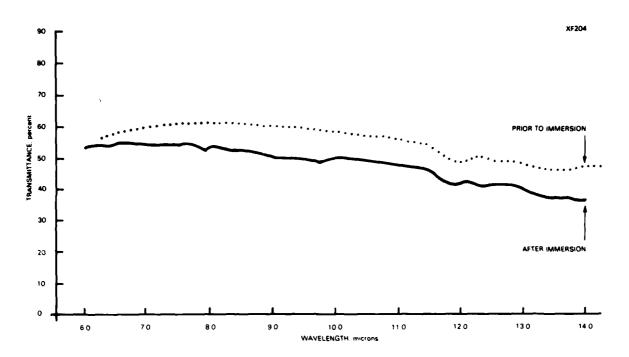


Figure 25. Transmittance of a 0.25-inch-thick germanium specimen with the Optic Electronic XF 204 antireflection coating on the sea face, both before and after 4 months' exposure to seawater in San Diego Bay.

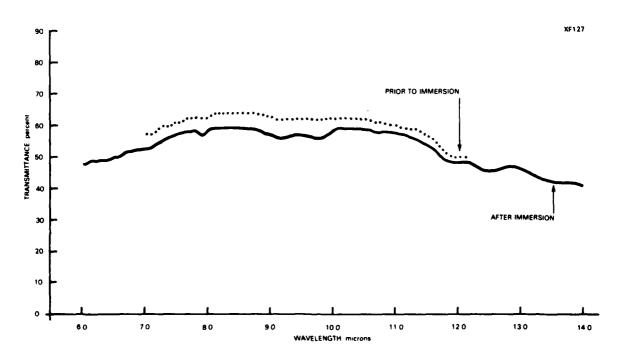


Figure 26. Transmittance of a 0.25-inch-thick germanium specimen with the Optic Electronic XF 127 coating on the sea face, both before and after 4 months' exposure to seawater in San Diego Bay.

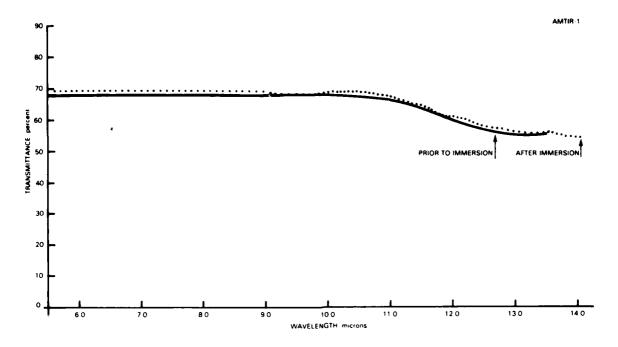


Figure 27. Transmittance of a 0.25-inch-thick bare specimen of AMTIR-1 chalcogenide glass, both before and after 4 months' exposure to seawater in San Diego Bay.

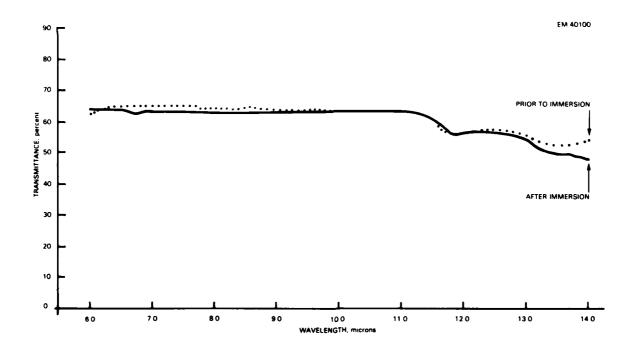


Figure 28. Transmittance of a 0.25-inch-thick germanium specimen with the Exotic Materials 40100 antireflection coating on the sea face, both before and after 4 months' exposure to seawater in San Diego Bay.

Similarly, the specimen coated with the Optic Electronic XF 202 dropped in transmittance after testing by less than 5% and only in the upper end of the wavelength range. The transmittance averaged 52% both before and after ocean exposure in the 6- to-9-micron-wavelength range (figure 29). The transmittance then gradually dropped to an average of 40% at the upper end of the wavelength range.

The transmittance curves of the Optic Electronic XF 203 and XF 205 coated specimens are very similar also. Both showed a slight drop in transmittance after seawater exposure above 8.5-micron wavelength. The transmittance gradually dropped more as the wavelength increased, to a maximum of a 9% drop at 14-micron wavelength for the XF 203 and an 8% drop at 14-micron wavelength for the XF 205. After immersion in seawater both specimens averaged 58% transmittance midrange, trailing off to about 43% transmittance at 14-micron wavelength (figures 30 and 31).

The specimen coated with the Optic Electronic XF 206 showed an unusual trace, depending upon the spot on the specimen at which the testing took place. The trace, when taken at certain locations, would have a pronounced sinusoidal oscillation, while at other locations this oscillation was largely damped out. It is postulated that this varying oscillation is the result of unequal thickness in the coating layer, which causes optical interference at the specimen-coating interface. It was decided to take transmission measurements both at a position displaying maximum amplitude of oscillation and at one displaying minimum amplitude of oscillation. These locations on the specimen were scribed for identification with a single mark at the point of maximum oscillation, and a double mark at the location of minimum oscillation.

At the single mark location (maximum oscillation) on the XF 206 coated specimen, the transmittance prior to seawater exposure and after exposure was not significantly changed. The average transmittance (averaged through the nodes of the oscillations) varied in a smooth curve from a high of 55% at the low end of the spectrum, to approximately 42% at 14-micron wavelength (figure 32).

At the double mark location (minimum oscillation) there was also no significant change in the average transmittance after exposure to seawater. The transmittance averaged 55% at the low end of the spectrum and dropped in a gradual curve to about 43% at 14-micron wavelength (figure 33). In figure 34, the curves of figures 32 and 33 are superimposed to show the common zero line of the oscillations.

The amplitude of oscillation decreased slightly at both locations after seawater exposure.

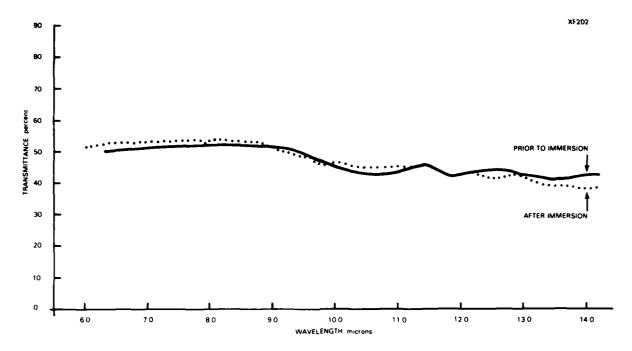


Figure 29. Transmittance of a 0.25-inch-thick germanium specimen with the Optic Electronic XF 202 antireflection coating on the sea face, both before and after 4 months of exposure to seawater in San Diego Bay.

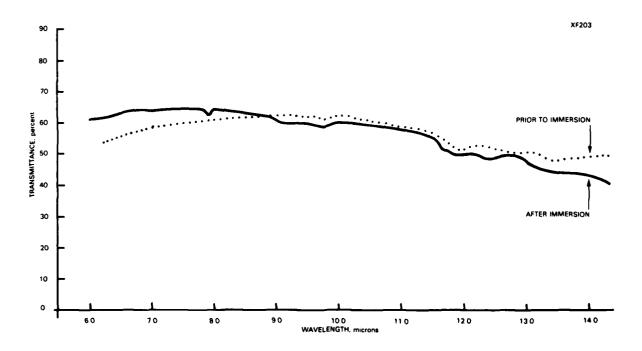


Figure 30. Transmittance of a 0.25-inch-thick germanium specimen with the Optic Electronic XF 203 antireflection coating on the sea face, both before and after 4 months of exposure to seawater in San Diego Bay.

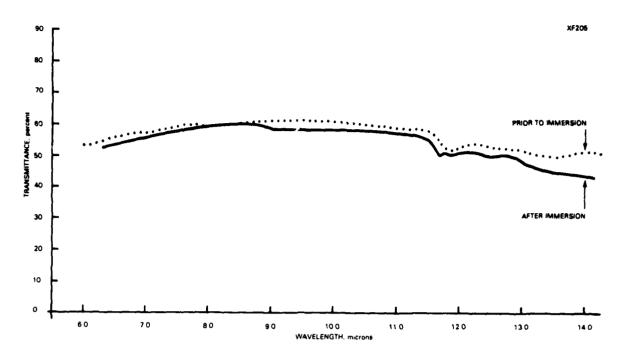


Figure 31. Transmittance of a 0.25-inch-thick germanium specimen with the Optic Electronic XF 205 antireflection coating on the sea face, both before and after 4 months of exposure to seawater in San Diego Bay.

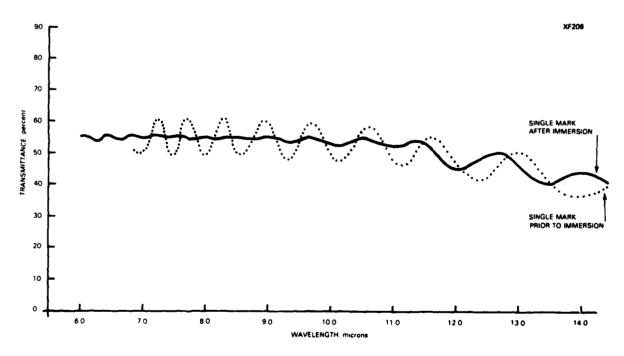


Figure 32. Transmittance of a 0.25-inch-thick germanium specimen with the Optic Electronic XF 206 coating on the sea face. The transmittance was tested in two places, both before and after 4 months of exposure to seawater in San Diego Bay. This curve is the transmittance at the single mark location.

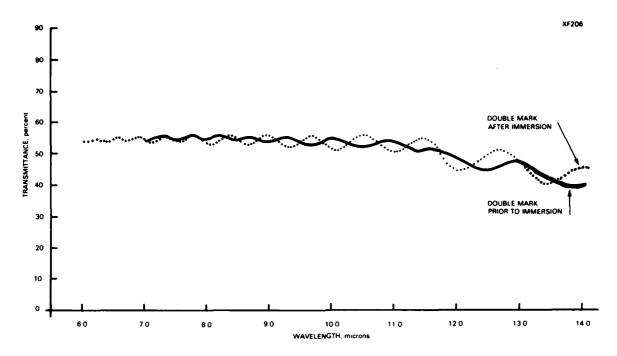


Figure 33. Transmittance of a 0.25-inch-thick germanium specimen with the Optic Electronic XF 206 coating on the sea face. The transmittance was tested in two places both before and after 4 months of exposure to seawater in San Diego Bay. This curve is the transmittance at the double mark location.

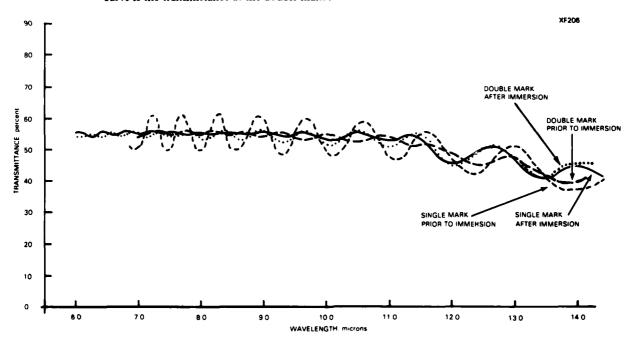


Figure 34. Transmittance of a 0.25-inch-thick germanium specimen with the Optic Electronic XF 206 coating on the sea face. The transmittance was tested in two places both before and after 4 months of exposure to seawater in San Diego Bay. The curves are superimposed here to show the common zero line of the oscillations.

CONCLUSIONS

- 1. The unprotected chalcogenide AMTIR-1 glass surfaces showed excellent resistance to seawater corrosion, with no measurable loss of transmission during the 130-day exposure to seawater.
- 2. The chalcogenide AMTIR-1 glass coated germanium specimen (the Optic Electronic XF 206 coating) showed excellent resistance to seawater corrosion, with no measurable loss of transmission during the 130-day exposure to seawater.
- 3. Of the antireflection coatings tested, the Exotic Materials multilayer durable antireflection coating 40100 showed the best results. This coating had no significant drop in transmittance after seawater exposure and exhibited only few minor pits on the surface.

RECOMMENDATIONS

TECHNICAL

- 1. Further research should concentrate on germanium windows with chalcogenide glass coatings, as this solution combines the advantages of germanium (massive germanium is stronger, harder, and more thermally conductive than massive chalcogenide glass) with the advantages of chalcogenide glass (chalcogenide glass is more resistant to seawater corrosion than germanium). Glass coatings have the potential of providing protection against corrosion for submersions in excess of one year.
- 2. The durable multilayer antireflection coating, Exotic Materials 40100, should be utilized on germanium windows that must provide and maintain transmittance of over 90 percent in the 8- to 12-micron range during submersions of up to 6 months.
- 3. Massive chalcogenide glass AMTIR-1 continues to be more effectively resistant to seawater corrosion than any known antireflective coating, and it shows no decrease in transmission after seawater exposure. Windows and lenses of this material can be employed without any coating on the wetted surface as the transmittance through a chalcogenide glass window, coated on the interior surface, exceeds 80 percent regardless of the length of submersion in seawater.
- 4. Other materials, besides chalcogenide glass, should be investigated for potential service as coatings. Carbon with diamond-like molecular structure appears to be a very promising candidate for this application. Germanium test specimens coated with carbon by Honeywell Technology Center are currently being evaluated by NOSC for their resistance to seawater.

REFERENCES

- 1. Naval Ocean Systems Center Technical Note 121,* Undersea Testing of IR Antireflective Coatings and IR Materials, by JN Ferrer, March 1977.
- 2. Naval Ocean Systems Center Technical Report 421, Resistance of Coated and Uncoated IR Windows to Seawater Corrosion, by JD Stachiw and SL Bertic, August 1979.
- 3. Naval Ocean Systems Center Technical Report (to be published), Resistance of Coated and Uncoated IR Windows to Seawater Corrosion, Phase III, by JD Stachiw and SL Bertic, July 1980.

^{*}NOSC TNs are informal documents intended chiefly for internal use.